Unprecedented electron deficient bridging between zinc atoms by boron atoms of *nido*-carborane anions: preparation, crystal and molecular structure of the dimer [(*nido*-$C_2B_9H_{11}$)$ZnNMe_3$]$_2$

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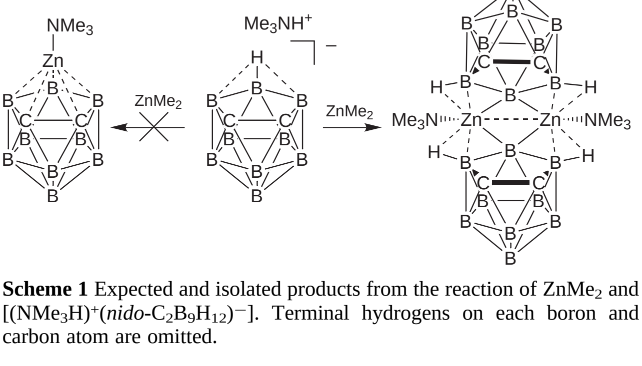
The alkane elimination reaction between $ZnMe_2$ and [$(NMe_3H)^+$(*nido*-$C_2B_9H_{12}$)$^-$] gives the macropolyhedral dimer [(*nido*-$C_2B_9H_{11}$)$ZnNMe_3$]$_2$, containing an unprecedented planar diamond-shaped Zn_2B_2 ring at its core.

The capacity of the *nido*-carborane anion $[C_2B_9H_{11}]^{2-}$ to bond cationic metallic units at sites on its open pentagonal face that reflect the frontier orbital characteristics of the metallic cations has long been recognised.[1] The σ^2,π^4 arrangement of the frontier orbitals of $[C_2B_9H_{11}]^{2-}$ is similar to those of the cyclopentadienyl, $(C_5H_5)^-$, and imido, RN^{2-}, ligands.[2] Both $[C_2B_9H_{11}]^{2-}$ and RN^{2-} act as 4 electron LX_2 ligands.[3] Metallic residues that are isolobal with BH^{2+} can bond η^5 to the face, and so effectively complete the *closo*-metallacarborane. It has been recognised that metal fragments with full, or almost full, d shells tend to occupy 'slipped' positions over the open face, even though the metal fragment formally has the three vacant orbitals of a BH^{2+} unit (one radially, two tangentially oriented).[4] Coordination in an η^1 mode is also observed when the metal fragment has fewer than 3 vacant orbitals, as in $[(\eta^1\text{-}C_2B_9H_{11})SnPh_3]^-$.[5] Alternative cluster geometries may also be observed even when the metal fragment has three vacant orbitals but is not isolobal with HB^{2+}.[6]

Noting that the only structurally characterised zinc borane species are a number of tetrahydridoborate complexes,[7] ionic compounds containing the $[Zn(B_{10}H_{12})_2]^{2-}$ anion,[8] and small zinc boranes,[9] and that complexes of boranes or carboranes[10] with group 2[11] or group 12 metals are rare (except for linear complexes of Hg^{2+}), we explored the reaction‡ between [$(Me_3NH)^+$(*nido*-$C_2B_9H_{12}$)$^-$] and $ZnMe_2$, which by loss of two moles of methane was expected to afford a monomeric icosahedral metallacarborane $Me_3N\text{-}ZnC_2B_9H_{11}$, Scheme 1. The units $Me_3N\text{-}Zn^{2+}$ and HB^{2+} are formally isolobal, and so in principle HB^{2+} units of borane clusters might be expected to be replaced by $Me_3N\text{-}Zn^{2+}$ units. The analogous beryllium complex, $[Me_3N\text{-}BeC_2B_9H_{11}]$, is believed to be isostructural and isoelectronic with *closo*-$C_2B_{10}H_{12}$.[12] The stoichiometry of our product was indeed as expected; however, an X-ray crystallographic study§ has shown it to have an alternative remarkable macropolyhedral dimeric structure, [(*nido*-$C_2B_9H_{11}$)$ZnNMe_3$]$_2$ **1**, shown in Fig. 1. Although the molecule has approximate C_{2v} molecular symmetry it has no crystallographically imposed symmetry. Two *nido*-$C_2B_9H_{11}$ fragments are connected through the unique boron atoms of the *nido* carborane residues and a $Me_3NZnZnNMe_3$ unit, in which the two zinc atoms are at a separation of 2.800(1) Å (*cf.* 2.665 Å for the shortest Zn–Zn distance in metallic Zn). The bonding of these boron atoms (coordination number 7) and of the zinc atoms (coordination number 8) are we believe unprecedented, and involve a planar diamond-shaped Zn_2B_2 ring system [angles at Zn 108.1(1)° and 105.5(1)°; two equal angles at B 73.2(1)°]. This is reminiscent of the 3-centre 2-electron (3c2e) bonds in the M_2C_2 ring systems of electropositive metal alkyls, as in Al_2Me_6,[13] or $(BeMe_2)_n$,[14] with characteristically acute angles at the alkyl carbon and obtuse angles at the electropositive metals. By contrast, zinc alkyls, ZnR_2 (R = Me, Et, Pr^n) are monomeric by gas-phase electron diffraction,[15] although in the solid state, diphenyl zinc is dimeric, $[(C_6H_5Zn)_2(\mu\text{-}C_6H_5)_2]$ [Zn–Zn = 2.685 Å], with unsymmetrical bridges, assigned to σ-covalent and π-dative bonds.[16] The Zn–Zn separations observed in amide-bridged $[(MeZn)(\mu\text{-}NPh_2)]_2$ (2.913 Å),[17] chloride-bridged $[Zn_2Cl_6]^{2-}$ (typically 3.06 to 3.3 Å)[18] and other electron-precise species, are longer than that in **1**.

In addition to the Zn_2B_2 ring the coordination about each zinc atom is completed by one NMe_3 ligand and interaction of a pair of B–H bonds with each zinc atom. Since Me_3N-Zn is isolobal with BH, compound **1** would be isolobal with the (unknown) species $C_4B_{20}H_{24}$ and $[B_{24}H_{24}]^{4-}$. The closest known carborane is $C_4B_{18}H_{22}$, which contains two $C_2B_9H_{11}$ residues directly fused.[19] Other clusters distantly related to **1** include *syn*-$B_{14}H_{20}$[20] and *anti*-{$[Pt(PMe_2Ph)]_2$(*nido*-B_6H_9)$_2$} containing



Scheme 1 Expected and isolated products from the reaction of $ZnMe_2$ and [$(NMe_3H)^+$(*nido*-$C_2B_9H_{12}$)$^-$]. Terminal hydrogens on each boron and carbon atom are omitted.

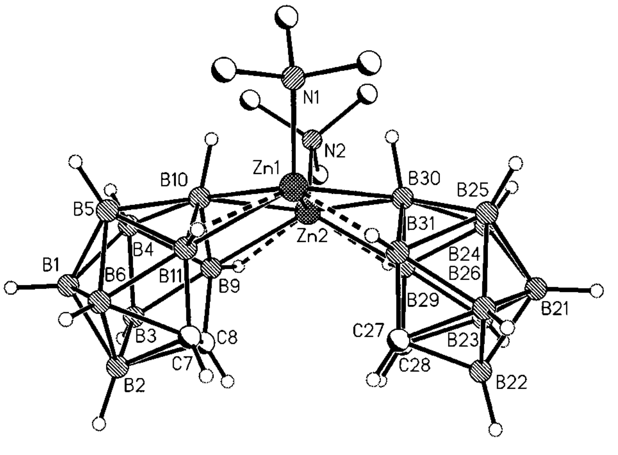


Fig. 1 A view of the 'head-set' or 'ear-muff' molecular structure of [(*nido*-$C_2B_9H_{11}$)$ZnNMe_3$]$_2$, showing the adopted atom numbering scheme. Hydrogen atoms on the NMe_3 ligands are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–B(10) 2.315(3), Zn(1)–B(11) 2.177(3), Zn(1)–B(30) 2.340(3), Zn(1)–B(31) 2.165(3), Zn(2)–B(9) 2.160(3), Zn(2)–B(10) 2.380(3), Zn(2)–B(29) 2.163(3), Zn(2)–B(30) 2.352, Zn(1)–N(1) 2.065(2), Zn(2)–N(2) 2.062(2), Zn(1)–Zn(2)–N(2) 127.30(8), Zn(2)–Zn(1)–N(1) 126.87(6); other values are given in the text.

square planar 16 electron platinum.[21] There is some structural resemblance to the μ-allyl ligand bridging two metal atoms in $[W_2(\mu;\eta^3\text{-}C_3H_5)_2(NMe_2)_4]$,[22] though in this allyl complex the central W_2C_2 ring is far from planar.

The geometry of the Zn_2B_2 ring at the centre of the structure of **1** prompts us to interpret the metal–ligand bonding primarily in terms of two 3c2e Zn–B–Zn bonds. However, it should be noted that there is a roughly tetrahedral coordination about each metal atom if one counts the other metal atom, and trimethylamine ligand, and two BH units (connected to the bridging B atom) as defining the ligand sphere and ignores the bridging boron atoms. It is clear that a rationalisation of this structure in terms of a localised bonding model has its limitations. We are undertaking more detailed investigations of the bonding in $[(nido\text{-}C_2B_9H_{11})ZnNMe_3]_2$ using molecular orbital methods, and these will be reported in a subsequent publication.

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Notes and References

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‡ *Selected data* for **1**. A stirred suspension of $[nido\text{-}C_2B_9H_{12}][NMe_3H]$ (0.288 g, 1.5 mmol) in toluene (20 ml) was treated dropwise with Me_2Zn (0.75 ml of 2 M solution in toluene, 1.5 mmol). After stirring for 18 h the solution was briefly refluxed and filtered whilst hot. Slow cooling to room temperature gave three crops of colourless crystals of $[(nido\text{-}C_2B_9H_{11})ZnNMe_3]_2$. Total yield 1.00 g, 96%. δ_H (300 MHz, $[^2H_5]$pyridine, $^1H\{^{11}B\}$) 2.57 (2H, BH), 2.44 (1H, BH), 2.37 (2H, BH), 2.27 (2H, BH), 2.07 (9H, NMe_3), 1.88 (1H, BH), 1.37 (1H, BH), 1.24 (2H, CH). δ_B (96.2 MHz, $[^2H_5]$pyridine) −16.3 (5B), −21.5 (2B), −32.3 (1B), −38.5 (1B). (Found: C, 36.3; H, 7.9; N, 4.9. $C_{10}H_{40}N_2B_{18}Zn_2(C_7H_8)_{1.35}$ requires C, 36.6; H, 8.0; N, 4.4%.)

§ *Crystal data* for $[(nido\text{-}C_2B_9H_{11})ZnNMe_3]_2\cdot1.5(C_7H_8)$: $C_{20.5}H_{52}B_{18}N_2Zn_2$, M = 651.96, triclinic, space group $P1$, a = 10.528(3), b = 10.915(3), c = 16.612(4) Å, α = 102.677(4), β = 96.566(4), γ = 107.892(4)°, U = 1738.0(7) Å^3, Z = 2, D_c = 1.246 Mg m^{-3}, μ = 1.398 mm^{-1}, 7914 unique data, 444 refined parameters, $1.28 < \theta < 27.48°$, R_1 = 0.0414, wR_2 = 0.1055 [all data]. X-Ray diffraction data were collected on a Siemens SMART CCD diffractometer at 150 K. Data Collection Software, SMART, Ver. 4.050, 1996, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA. Data Reduction Software, SAINT, Version 4.050, 1996, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA. Interactive Molecular Graphics, SHELXTL 5.04/VMS, 1995, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA. One of the toluene solvates and the NMe_3 ligand containing atom N(2) each display disorder of their constituent carbon atoms. For the amine ligand only the major component is shown in Fig. 1. CCDC 182/937.

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